ChemMatCARS

Surface Program at ChemMatCARS:

Science, Instrumentation and User Support

Binhua Lin

with

Mati Meron, Jeff Gebhardt, Tim Graber and Dave Schultz

and CARS technical group (Harold Brewer, Mike Bolbat, Guy Macha and Jay VonOsinski)

Surface Local Interest Group March 14, 2005

Surface X-ray Scattering Studies of Liquid Surface/Interfacial Phenomena

OUTLINE

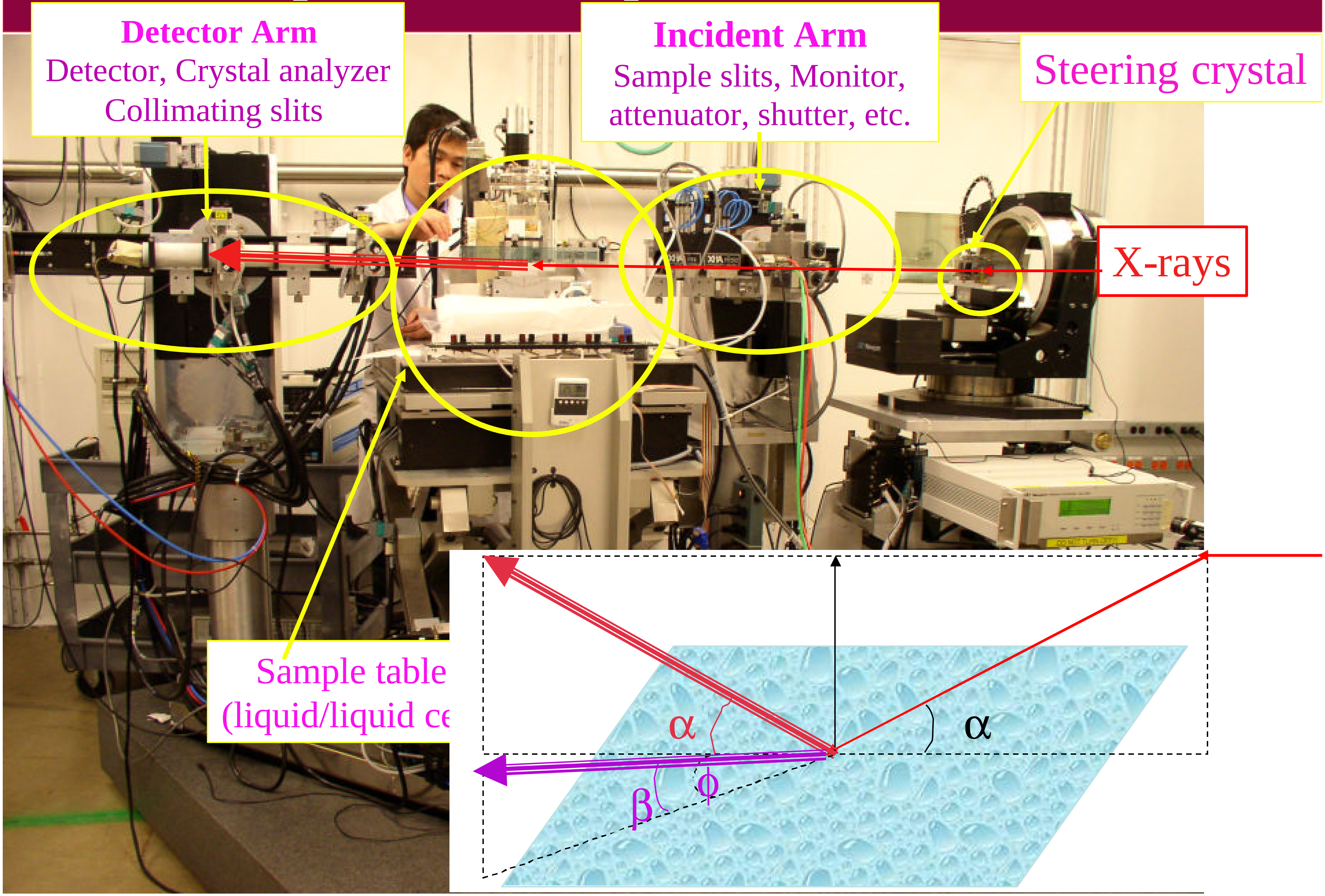
- Scientific Background
  - Liquid surface/interfacial systems
  - X-ray surface sensitive techniques
- Instrumentation-Liquid surface spectrometer
  - Design and Capability
  - User support infrastructure
- User Science Programs
  - User groups
  - Highlights of user experiments

Liquid Interfacial Systems

- **Experimental Systems**:
  - Monolayers at air-liquid and liquid-liquid interfaces
  - Liquid metal-X interfaces
  - Liquid-liquid interfaces: aqueous-organic, aqueous-aqueous
  - Surfaces of complex fluids: polymers, liquid crystals, lipids, etc.
  - Solid-liquid and Soft-Solid interfaces *(Dave Schultz leads)*
- **Basic Scientific Issues:**
  - Characterization of surface/interfacial structure on the length scale of Å - μm.
  - Understanding the effect of surface/interface on the ordering, interactions, and dynamics of the molecules.
  - Model two-dimensional systems

X-ray surface sensitive probes	Interfacial properties	Status @15IDC
Specular reflectivity	Electron density profile normal to surfaces	Working/ upgrading (V focus)
Grazing incident Bragg diffraction	Ordering (disorder) within interfacial plane	Working/ upgrading (CCD, analyzer, 2nd detector arm)
Off-specular diffuse scattering	In-plane inhomogeneity of the interfaces	Working/ upgrading
Standing wave fluorescence spectroscopy	Depth profiles of metal particles in liquid/solid films	Working/ upgrading (Dave)
Combination of x-ray scattering with optical microscopy *in situ* (BAM&FM)	Complementary real space images and q-space info	Developing (with Prof. Ka Yee Lee)
Coherent static/dynamic x-ray scattering	Detailed interfacial structure and diffusion within or near interfaces	Developing (With Prof. Sunny Sinha)

Liquid Surface Spectrometer 15ID-C



Spectrometer Design--Main Challenges

Small vs. large samples

- **Heavy load**
- **Large travel**
- **Precise motion**

•Designed and Developed with in house experts

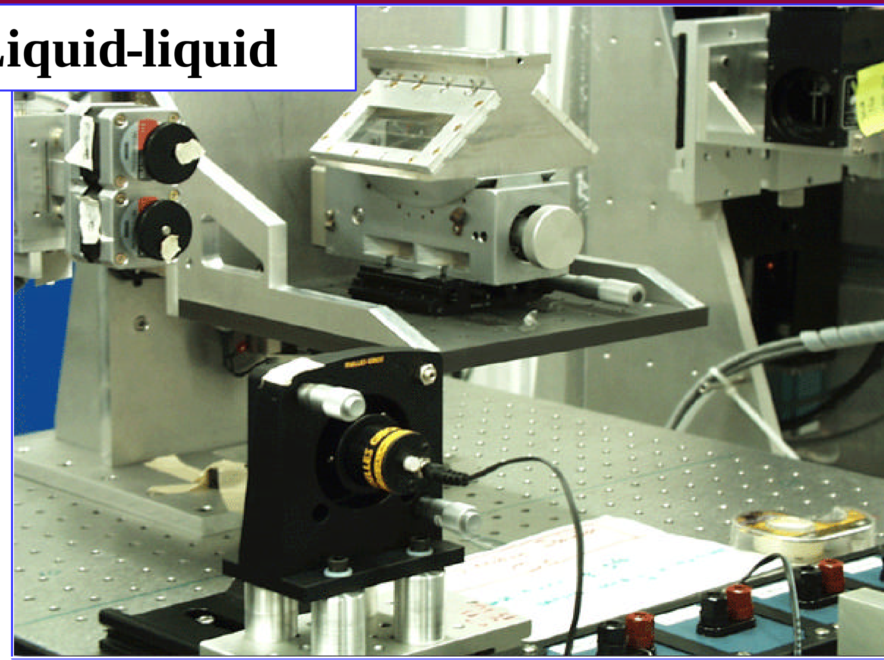
–Based on the design of the liquid spectrometer at X19C (NSLS)

(Binhua Lin, Mati Meron, Mark Schlossman, Jeff Sundwall, Jim Viccaro)

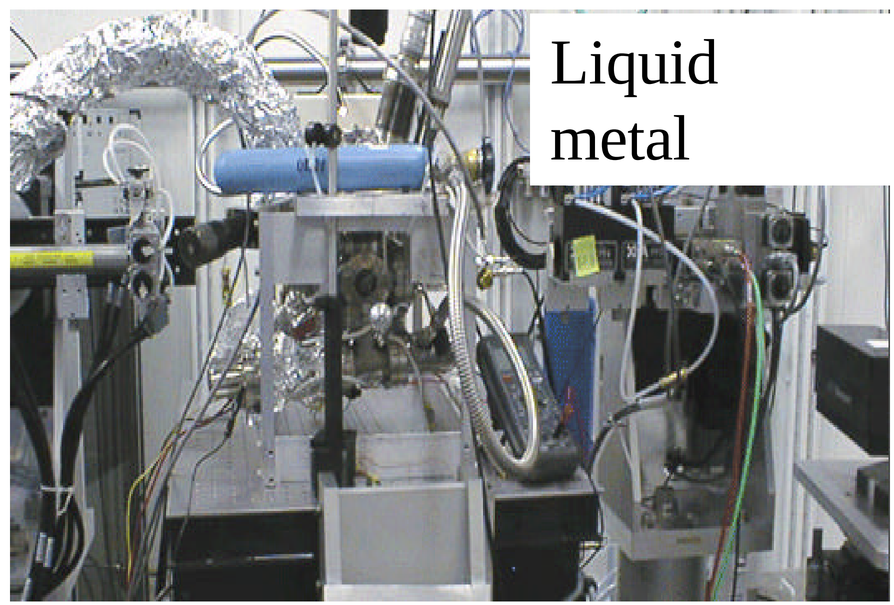
–Complex x-ray tracking geometry--beam propagation error analysis (Mati Meron)

–Complex electronics—30 motors on the spectrometer (Jeff Gebhardt)

Liquid-liquid



Liquid metal



Liquid Surface Spectrometer @15IDC	Performance
Energy Range	**8keV-30keV**
Energy Accuracy ($\Delta E/E$)	$\sim 10^{-4}$
Specular Reflection @ E~20 keV 1) q_z range 2) Δq_z (with slits) 3) Δq_z (with channel cut analyzer)	 **4.5Å^{-1}** (1.4Å in real space) 10^{-3}Å^{-1} Under commissioning
Grazing Incident Diffraction @ E~17.7keV 1) q_{xy} range (for θ_{xy} = 90^o) 2) $\Delta\theta_{xy}$ (with Soller slits) 3) $\Delta\theta_{xy}$ (with **channel cut analyzer**)	 12 Å^{-1} 0.08 deg Under commissioning
Off Specular Reflection @ E~17.7keV 1) q_z range 2) Δq_z (with slits) 3) Δq_z (with channel cut analyzer)	 2.5 Å^{-1} (α~0.2^o, β=16^o) 10^{-6} Å^{-1} Under commissioning
Sample table specification 1) Load 2) Travel (vertical direction) 3) Precision	 250kg 400mm <± 2μm

Infrastructure for User Support

- **Laboratories, equipment, supplies:**
  - Chemistry, electronics, vacuum facility, machine shop, setup space
- **Technical support:**
  - Experimental: Binhua, Mati, Jeff, Dave
  - User support software (SPEC, IDL, EPICS): Mati, Tim, Jeff, Dave
  - X-ray optics: Tim, Mati
  - Control, electronics: Tim, Jeff
  - Wet chemistry lab supplies, waste control: Binhua, Dave, David Cookson
  - Setup, mechanical, vacuum, emergency repair: Harold Brewer, Mike Bolbat, Guy Macha, Jay VonOsinski and Frank Westferro
  - Photo records: John Shick
  - Central commander (panic button): Jim Viccaro

User Groups

The Users

- Stuart A. Rice (U of Chicago)
  - Liquid Metal/Alloys
- Peter Pershan (Harvard)
  - Liquid Metal/Alloys
- Mark Schlossman (U of IL at Chicago)
  - Liquid/liquid interfaces
- Ian Gentle (Queensland, Australia)
  - Langmuir monolayers of porphyrin salts
- Sunil Sinha (UCSD) & Metin Tolan (Dortmund, Germany)
  - Supercooled water
- Ka Yee Lee (U of Chicago)
  - Lipid/cholesterol mixtures

To Be Users

- Miriam Rafailovich (SUNY)
  - polymer melts and polymer nano-composites on the surface of water
- ChemMatCARS core group
  - Monolayers of metal nanospheres on the surface of water

Molecular structure at Nitrobenzene-Water interface

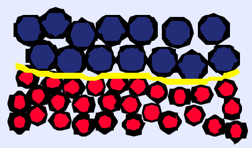
First structural measurements of polarizable liquid-liquid interfaces

Precursor experiments to investigate molecular scale effects in liquid-liquid electrochemistry

Address two issues:

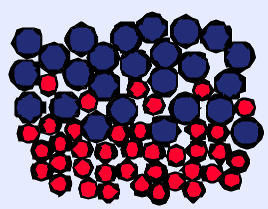
1. **Interfacial width** of pure interface due to

Capillary Waves



and/or

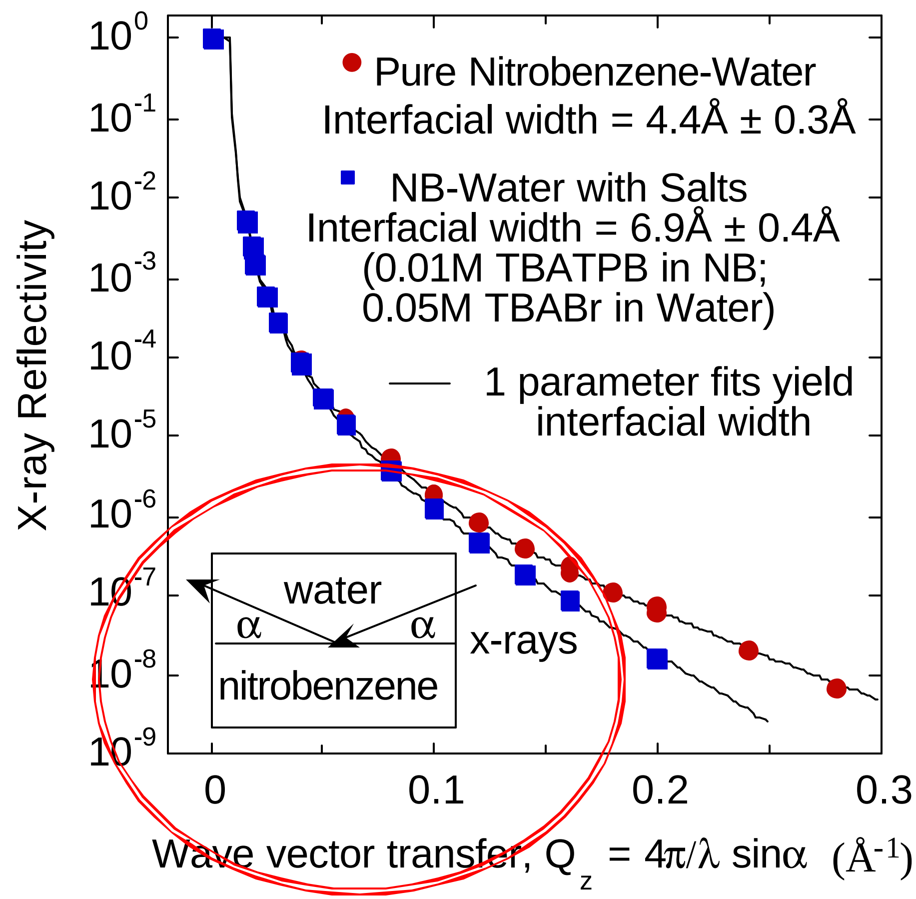
Interfacial Mixing?



- **Preliminary analysis consistent with capillary waves.**

2. **Interfacial electric field** alters molecular organization and elastic properties of interface

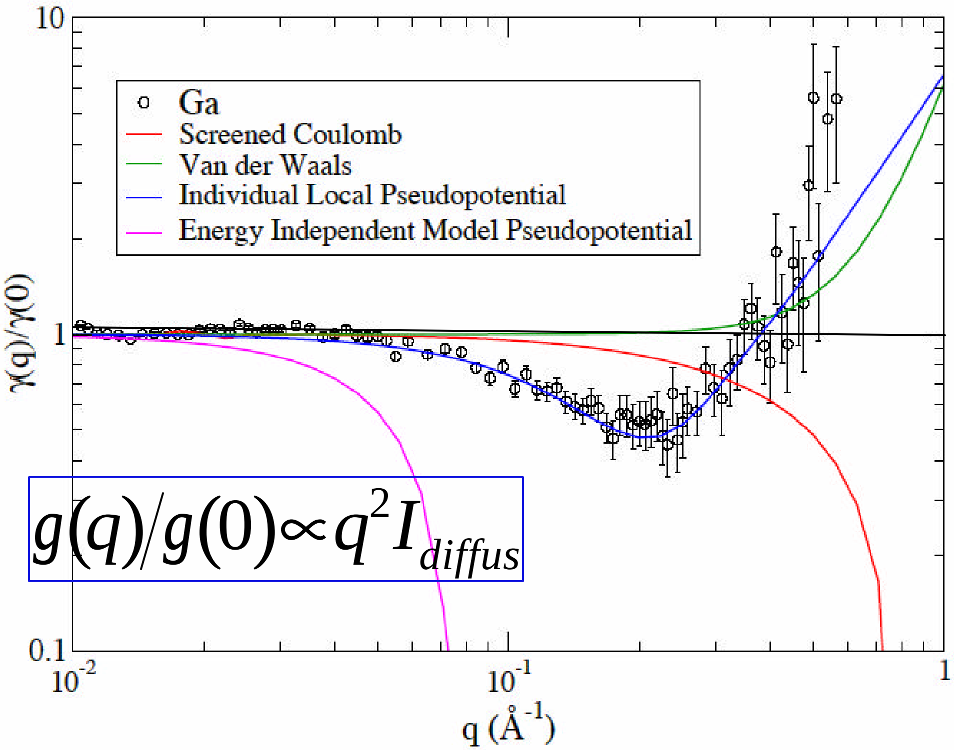
Polarizable Liquid-Liquid Interfaces



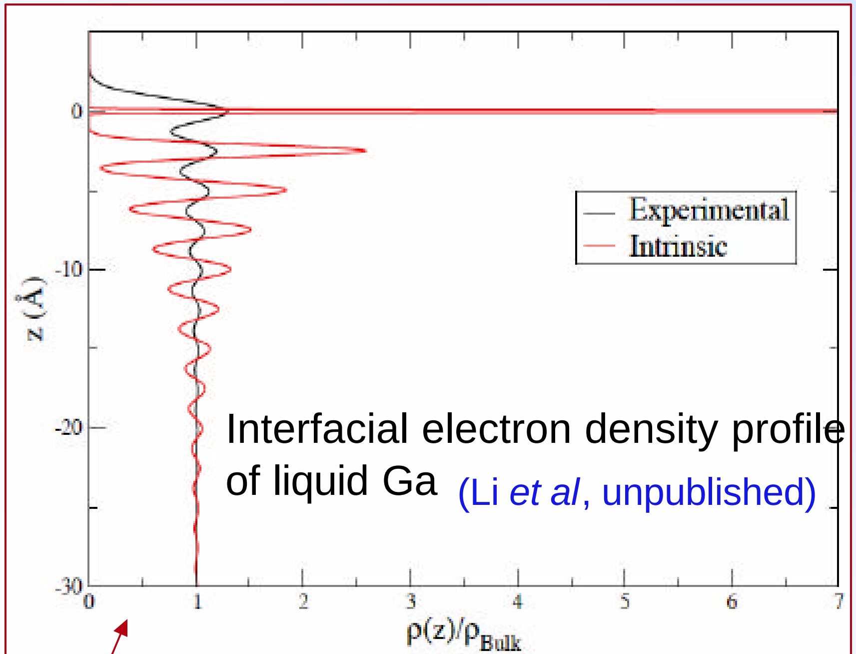
Faraday Discussions 129, 23, 2005(Schlossman's group, U of IL at Chicago)

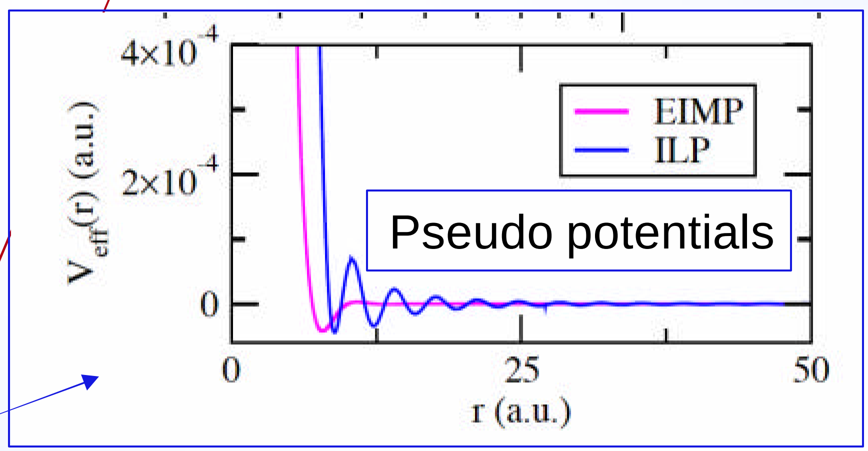
q-dependent surface tension of liquid gallium at 35ºC

Normalized *q*-dependent surface tension of Ga



$$g(q)/g(0) \propto q^2 I_{diffus}$$

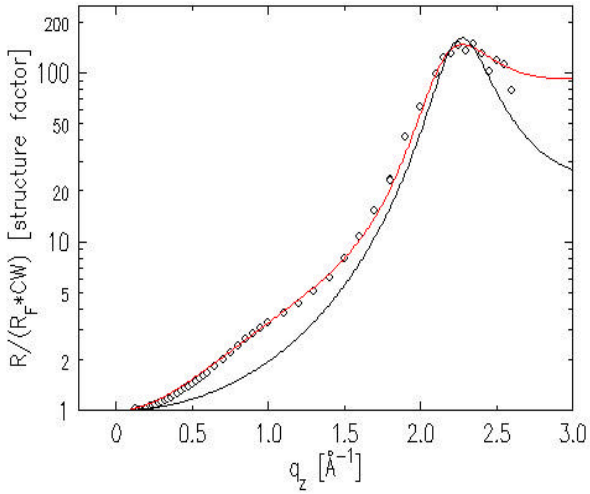


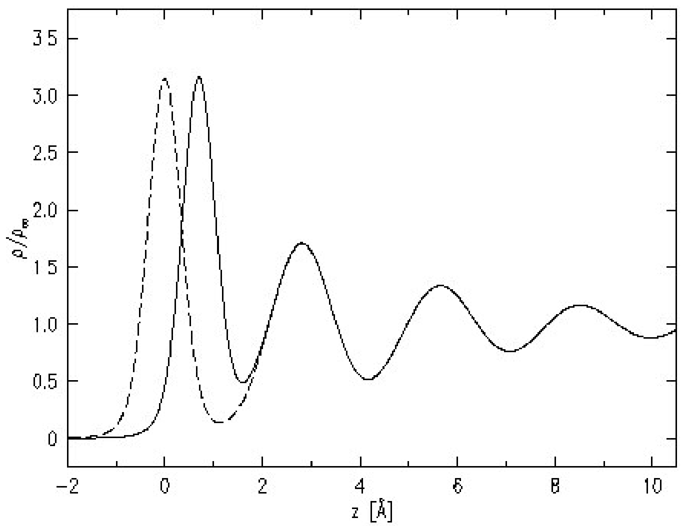


Comparison of the normalized *q*-dependent surface tension of Ga determined experimentally with that calculated using the Mecke-Dietrich formalism (PRE, 1999) with *a stratified intrinsic interfacial density profile* and *several model potentials*.

Rice's group (U of Chicago), *PRL*, **92**,136102 (2004)

Anomalous Layering at Liquid Sn Surface



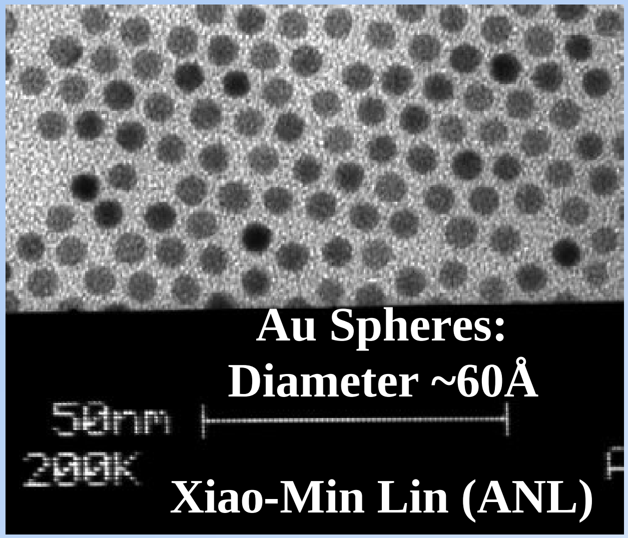


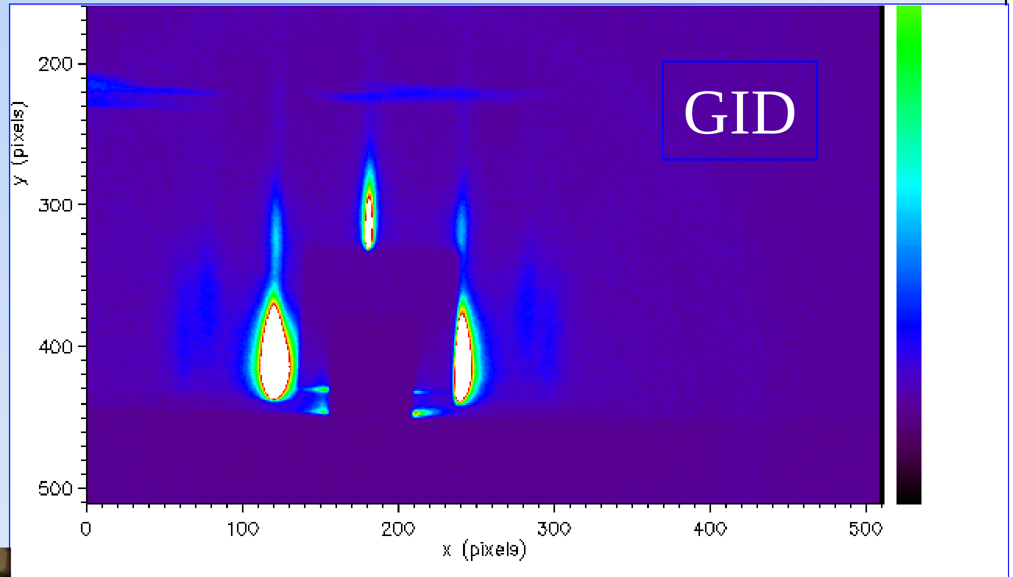
- X-ray specular reflectivity is a direct measure of a surface structure factor
- A peak in surface structure factor is associated with a surface-induced atomic layering, found in a number of metallic liquids
- A deviation from the classic layering behavior at low wave vectors found for liquid Sn is an unexpected feature, consistent with a densely packed atomic layer at the surface

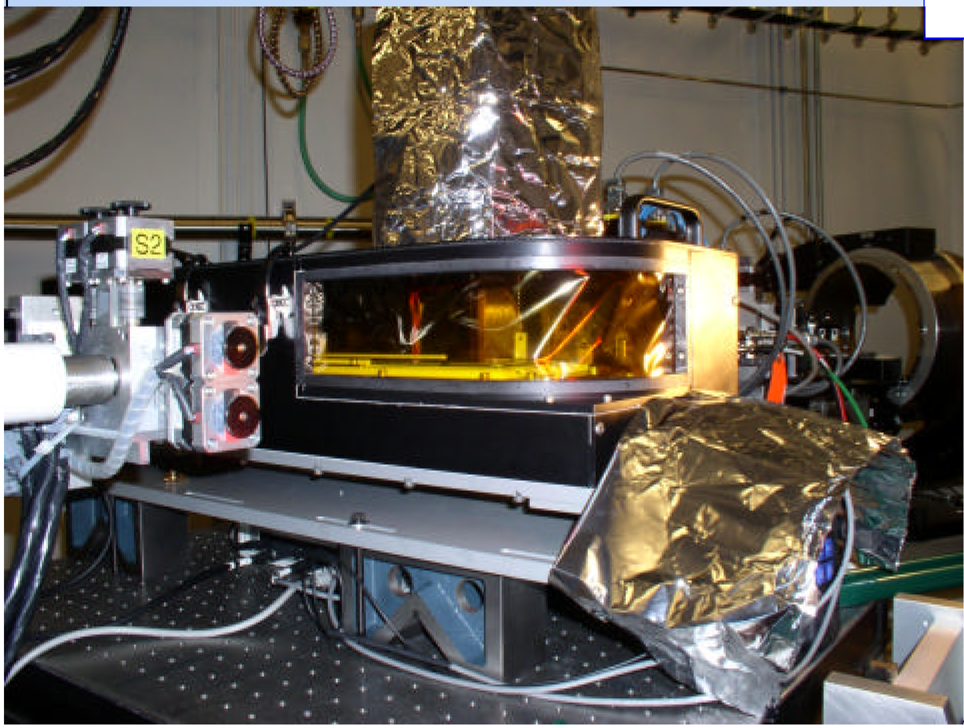
Shpyrko et al, *PRB* 70 224106 (Prof. Peter Pershan's group, Harvard)

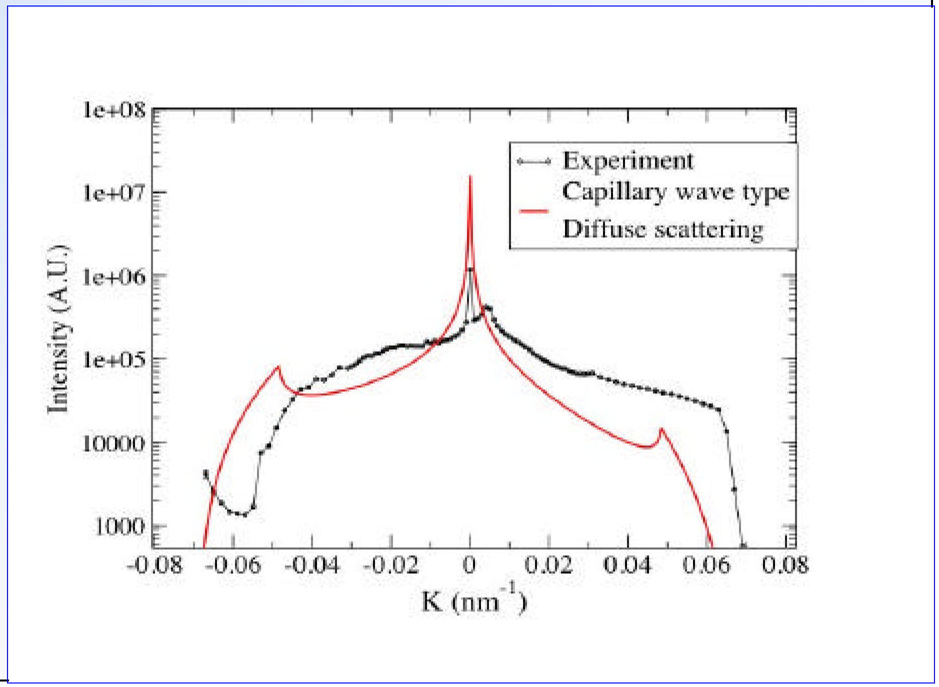
A monolayer of Au nanospheres on the surface of water

B. Lin, M. Meron, D. Schultz, J. Gebhardt, and J. Viccaro (ChemMatCARS)









The End

Solid Surface Scattering at 15-ID

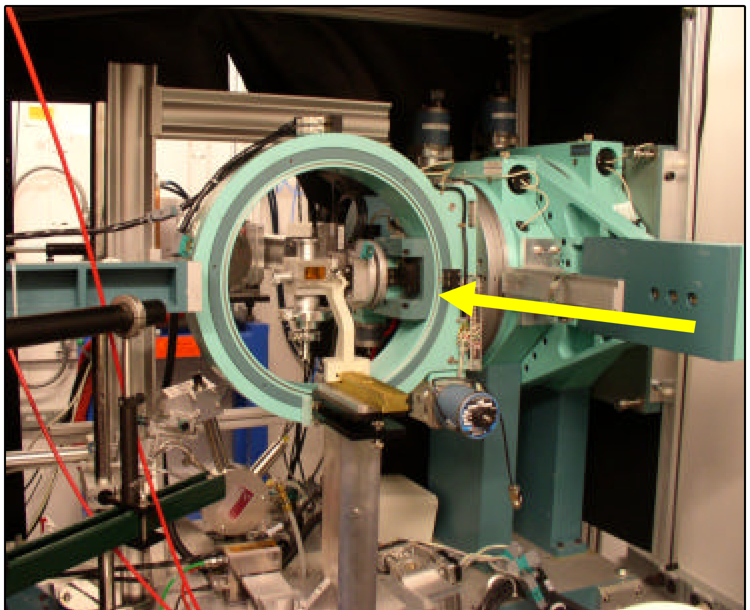
David Schultz

Emphasis on Soft Condensed Matter Films

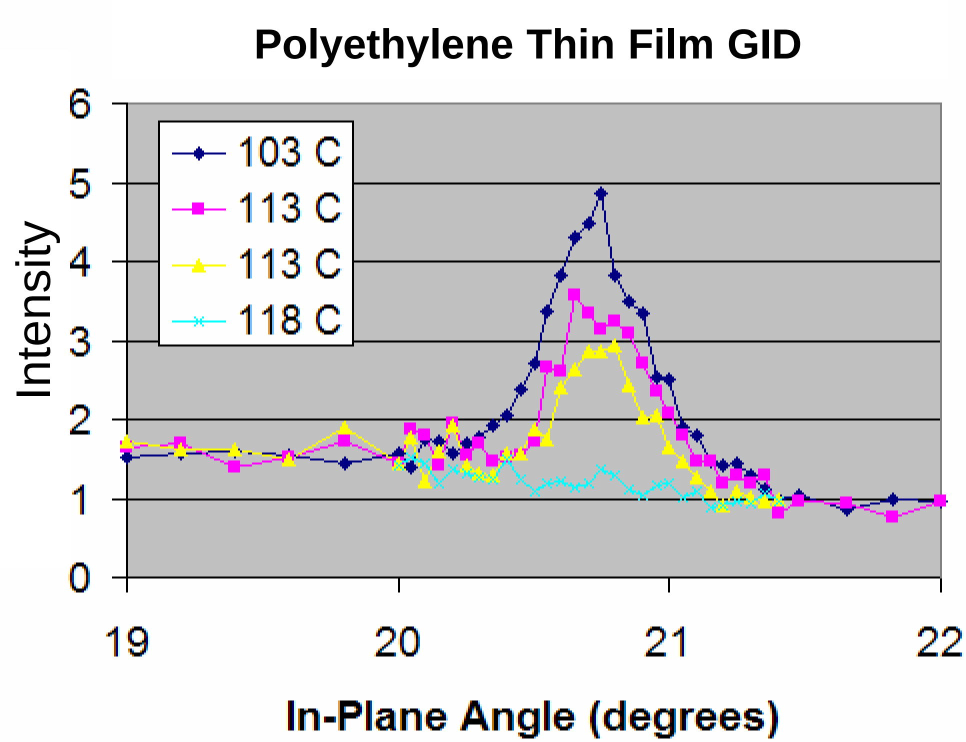
- **Polymer**
- **Biological**
- **Solid/liquid**

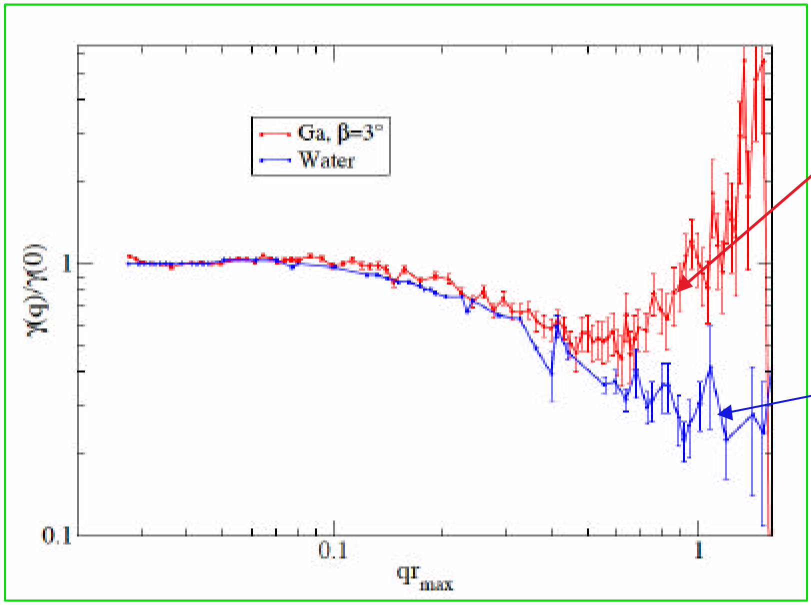
Techniques

XR, XDS, GID, GISAXS, XSW



Huber 4-circle shown with vacuum furnace for polymer GID





Normalized *q*-dependent surface tension of liquid Ga from x-ray surface diffuse scattering intensity

Normalized *q*-dependent surface tension of water from x-ray surface diffuse scattering intensity, agreed well with Mecke-Dietrich's *H(q)* using pair-potential and density profile appropriate for water surface (Fradin et al, Nature 2000)